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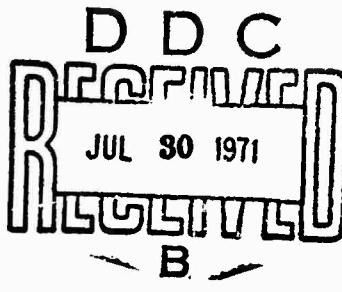
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## THERMAL ANALYSIS OF SEA WATER

Trudy Solyanoy Laboratorii  
(Transactions of Saline Laboratory),  
USSR Academy of Sciences, Central  
Saline Laboratory and All-Union  
Institute of Metallurgy, Issue 15,  
No 1, 1937, pp 5-23

K. E. Gitterman

Ocean water is a dilute solution of salts entering its composition. A single exception is calcium carbonate, and the question as to whether sea water is saturated or oversaturated by it has until now been a subject of scientific discussion. The question of obtaining any combination of salts from ocean water requires its enrichment by salt and the crystallization of salt from the concentrate derived. In a number of places with favorable climatic conditions, e.g. on the shores of the Black Sea and the Sea of Azov, ocean water is concentrated by natural evaporation in specially constructed basins. However, in certain geographic zones, (Scandinavian Peninsula, Northern Kray, the USSR Far East, etc.), the natural evaporation can not be achieved owing to unfavorable climatic conditions. The relatively low air temperature during the winter, at a considerable duration of it, raises the question concerning the possibility in these regions of a winter concentration of sea water by a method of natural freezing.

Primitive attempts to utilize the freezing-out of salt solutions have been undertaken repeatedly. For example, the salt works, having existed at Selenginskoye Ozero (Lake) (Siberia) operated only in winter, utilizing the under-ice lake brine [See Note] as a raw material ([Note]: Refer to the Laksman manuscript "Advance Notice Concerning Effects in Salt, Accomplished by Cold Frosts in Favor of the Salt Works in Lauriya," 1769. Leningrad Branch of Central Historical Archives).

There are a number of reports on the application of the freezing-out of brines at various plants in the Northern Kray, the Urals and Eastern Siberia: Seregovskiy [See Note 1], Totemskiy [See Note 1], Dedyukhinskiy [See Note 2], Ust'-Kutskiy [See Note 1], and Usol'skiy [See Note 3]. The Pomorskiye Salt Works having existed in the last century (formerly Kemskiy Uyezd) operated

only in winter, utilizing the under-water solutions of sea water, additionally frozen out in the holes along shore. There are reports in the literature [See Note 4] on the conduct in Norway from 1916-1919 of large experiments on obtaining cooking salt from sea water with the application of electric evaporators after a preliminary concentration of solution by the freezing-out technique. Unfortunately, the test results have remained unpublished ([Note 1]: K. Skal'kovskiy, Mining Journal, No. 4, 75-97, 1865. [Note 2]: G. Lyubarskiy, Mining Journal, No. 5, 1871. [Note 3]: N. Prikhozhan, Mining Journal, No. 1, 33-35, 1931. [Note 4]: Wenhart, Kali, No. 24, 372, 1939).

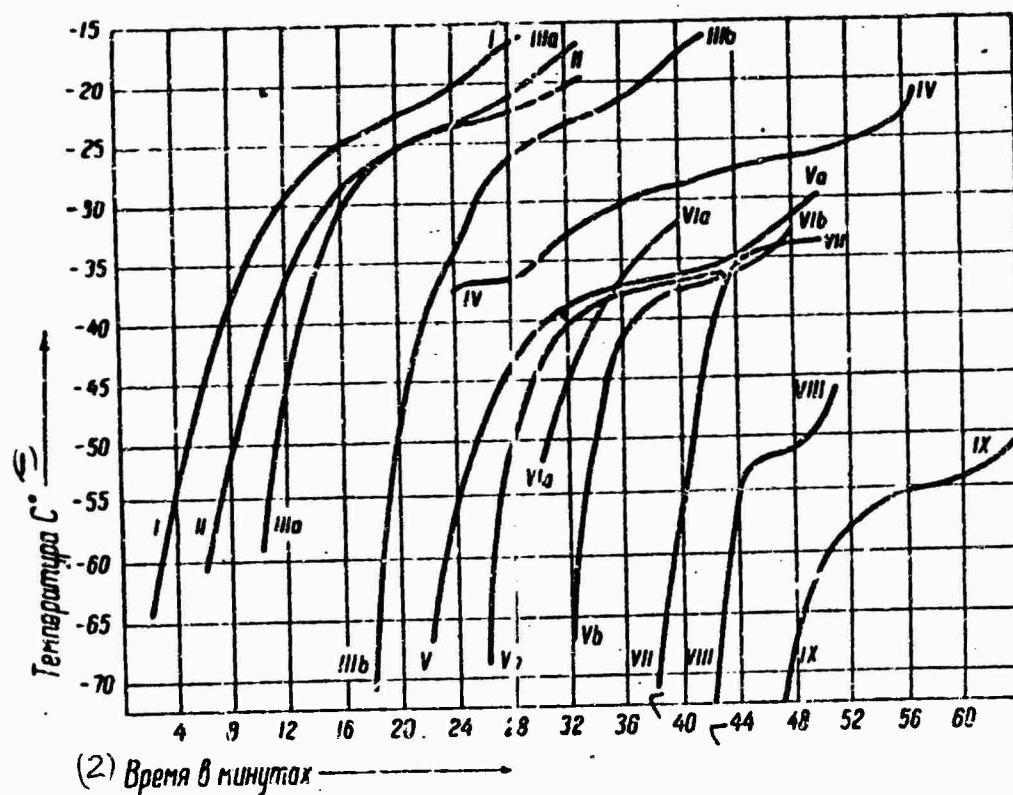


Fig. 1. Key: 1. temperature,  $^{\circ}\text{C}$ ; and 2. time expressed in minutes.

The physico-chemical studies concerning variations in the salt composition of sea water during its cooling were conducted chiefly in connection with the problems of oceanography.

A thermal analysis of sea water was conducted at the suggestion of Knudsen Ringer ([Note]: Ringer, Rapports et Procès-Verbaux des Réunions [in French], (Reports and Proceedings of Assembly), XLVII, 226, 1928. Verhandelingen Rijks Instituut Voor het Onderzoek der Zee (Transactions of Royal Institute for Investigation of the Sea), 1, 3-55, 1906). For the experiments, Ringer utilized the ocean water, prepared synthetically according

to the Dittmar analyses. We have presented in Fig. 1 the curves obtained by him for the heating of sea water concentrates frozen at low temperatures.

Curve I for concentrate with $t^{\circ}$ of freezing.....	-8°
" II "	" " " ..... -15°
" IIIa "	" " " ..... -10°.2
" IIIb "	" " " ..... -10°.2
" IV "	" " " ..... -25°
" Va "	" " " ..... -30°
" Vo "	" " " ..... -30°
" VIa "	" " " ..... -30°
" VIb "	" " " ..... -30°
" VIIb "	" " " ..... -30°
" VII for $MgCl_2$ solution of almost cryohydric composition	
" VIII for a concentration of $CaCl_2$ solution	
" IX for a synthetic solution corresponding to freezing-out to -50° and frozen at -80°	

Ringer established that the beginning of ice separation from sea water with a total salt content of 35°/oo corresponds to a temperature of -1°.91°C. Glauber's salt starts to separate at -8°.2. The chlorine content at this temperature is 68.9°/oo. At around -23°C, sodium chloride begins to crystallize. Magnesium chloride begins to separate at around -36° and calcium chloride crystallizes at -55°. As a result of the separation of Glauber's salt, the ratio  $Na_3/Cl$  decreases with a decrease in temperature (Table 1).

Table 1

(1) Temp., °C	-8.2	-9	-10	-12	-15	-20	-25	Примечание (?)
$\frac{SO_3}{Cl}$ . . . . .	0.118	0.080	0.053	0.036	0.024	0.012	0.002	
$\frac{SO_4}{Cl}$ . . . . .	0.143	0.096	0.063	0.043	0.029	0.014	0.008	Непрочет сам .
% выделение $SO_4$	0	32.3	55.0	69.5	79.7	89.8	94.2	(4)

Key: 1. Temperature, °C; 2. Remark; 3. % of separation of  $SO_4$ ; and 4. Our conversion.

In the freezing-out of 1,000 g of sea water with a total salt content of 35°/oo, we obtain the following relationship of the liquid and solid phases (Table 2).

The solid phase forming at freezing-out to -30° has the composition: 931.9g of ice, 20.23g of  $NaCl$ , 3.95g of  $Na_2SO_4$  and calcium carbonate.

Table 2

(1) Темпер. °C	-5	-8.2	-10	-15	-23	-30
(2) Жидкая фаза (г) . . .	429.5	284.5	234.0	186.1	134.9	43.95
(3) Твердая фаза (г) . . .	570.5	718.5	766.0	813.9	865.1	356.05
(4) $\text{Na}_2\text{SO}_4$ в твердой фазе (г) . . . .	0.0	0.0	1.84	3.00	2.68	3.25

Key: 1. Temperature, °C; 2. Liquid phase (g); 3. Solid phase (g); and  $\text{Na}_2\text{SO}_4$  in solid phase (g).

The composition of the liquid phase corresponding to this same temperature is:  $\text{MgCl}_2 = 117.0\%$ ;  $\text{NaCl} = 81.9\%$ ;  $\text{CaCl}_2 = 24.8\%$ ;  $\text{KCl} = 14.8\%$ ;  $\text{KBr} = 2.2\%$ ; and  $\text{Na}_2\text{SO}_4 = 0.9\%$ .

At a temperature of  $-53^\circ$ , Ringer investigated only the liquid phase containing:  $\text{CaCl}_2 = 257\%$ ;  $\text{MgCl}_2 = 250\%$ ;  $\text{NaCl} = 12\%$ ;  $\text{KBr} = 20\%$ ; and  $\text{NaBr} = 3\%$ .

From the Ringer data which have been presented, we can form a conclusion to the effect that during the freezing-out of sea water, the separation of calcium sulfate does not occur and the metamorphization of the solution proceeds only owing to the crystallization of sodium sulfate decahydrate (Glauber's salt). Therefore, the concentration of calcium ion in the solution increases continuously and the complete freezing of the system occurs near the cryohydric point of calcium chloride.

In recent years, in the chemical literature, reports have been published by Il'inskiy and Sagaydachnyi on a study of the polythermal areas of crystallization of Glauber's salt [See Note] ( $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ) and calcium chloride bihydrate [See Note 2 ( $\text{NaCl} \cdot 2 \text{H}_2\text{O}$ ) in the system  $\text{MgSO}_4 + \text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$  ([Note 1]: V. P. Il'inskiy and A. F. Sagaydachnyy, Journal of Russian Physical-Chemical Society, 10, 1929. [Note 2]: The same authors, Journal of General Chemistry, Vol. I, No. 5)].

The authors present a series of isotherms of this system and provide quantitative data of an intensive increase with a decrease in temperature in the area of crystallization of Glauber's salt owing to a reduction in the separation fields of magnesium sulfate and, to a lesser extent, of sodium chloride. Below a temperature of  $0^\circ\text{C}$ , there appears a field of sodium chloride bihydrate, increasing at a decrease in temperature, with a simultaneous reduction in the area of anhydrous salt crystallization. The composition of the system's solid phases is simplified considerably, since all of the double salts forming at temperatures above  $0^\circ\text{C}$  disappear.

Proceeding to a study of the process of freezing-out of sea water, we did not have access to the above-listed Ringer data, not reflected in the chemical literature, however the basic differences between our initial results and Ringer's observations compelled us to accomplish a more profound study along these lines.

As an initial solution for the freezing-out experiments, we utilized a synthetically prepared solution corresponding to ocean water in composition of basic salt components (according to Ful'd, Table 3).

Table 3

(1)								
NaCl	KCl	KBr	MgCl <sub>2</sub>	MgSO <sub>4</sub>	CaSO <sub>4</sub>	CaCO <sub>3</sub>	Cymna coneB	H <sub>2</sub> O
2.592	0.065	0.009	0.322	0.212	0.123	0.010	3.334	96.67

Key: 1. Total salts.

The study was conducted by two methods: dynamic, by way of deriving in curves for the cooling for various concentrations of the above-listed solution, and static, consisting of a step-by-step freezing-out of the original solution. For the derivation of cooling curves, we utilized a modified Beckman device incorporating mechanical vertical mixing, being achieved by means of a crankshaft device. Temperature was measured with a thermometer with a scale division of 0.1°, which established the measurement accuracy of ±0.02.

For the obtainment of stable bending points on the cooling curves, the observance of the following conditions has primary significance: 1) constancy in cooling range in the process of the experiment, 2) sufficient speed of mixing and 3) simultaneous introduction of seeding.

The first condition is accomplished by means of a gradual reduction in temperature in the tank being cooled, with a device having sufficient air insulation. With the preliminary tests, it was established that it is most feasible to determine the cooling rate by a temperature drop of 0°.1 per minute. At a more rapid conduct of the experiment, one obtains considerable supercoolings and a diffused bending on the temperature-time curve. In conformity with the selected cooling rate, one finds the mixing rate of the solution, which can be established only by preliminary tests in reference to the design of the mixer and dimension of the vessel. In his report on supersaturated salt solutions, Fisher [See Note] demonstrated the influence of the mixing rate on the extent of the solution's supersaturation: only at extremely rapid, turbulent mixing (more than 3,000 revolutions of the mixer) does the amount of supersaturation (and consequently of supercooling) become independent of the mixing rate ([Note]: Fisher, Investigation of Supersaturated Salt Solutions, St. Petersburg, 1912). In the same report, the author

establishes the so-called "period of induction", i.e. the time span from the instant of introducing the salt seeding into the supersaturated solution to the beginning of crystallization. At high mixing rates, this period depends on the extent of supersaturation, test temperature and nature of salt. According to Van't-Goff, salts form supersaturated solutions the more easily, the higher their product of valency. Our observations indicate that for finding the inflection point corresponding to the separation of Glauber's salt, it is advantageous to introduce the seeding 6-7 minutes prior to the start of crystallization, and for sodium chloride hydrate, 2-3 minutes prior to the beginning.

It is interesting to note that to the extent that it is difficult to obtain supercooled solutions of sodium chloride above 0°, we find the proportionate supercoolings of its solutions in the zone of low temperatures. This can be explained by the increased hydration of NaCl molecules below 0°C.

It is very difficult to obtain an inflection point for ice without a considerable supercooling. We can assume that ice has a large period of induction and the seeding should be introduced 10-12 minutes prior to the beginning of separation, but during this time interval, the "ice inoculation" increases, while the incidental substance isomorphic with the ice will dissolve.

The procedure involved in the step-by-step freezing-out of sea water consisted in the cooling of the solution to such a temperature at which there was established a ratio of solid and liquid phases advantageous for analytical purposes. Based on the composition of the liquid phase, we prepared a new solution which was frozen out at a lower temperature, and so forth. The taking of samples was accomplished with a pipet equipped with a collodion filter (filtering paper soaked with an alcohol-ether solution of collodion). The analysis of solutions was conducted according to the usual procedure: Cl<sup>-</sup>--by titration according to Mohr, SO<sub>4</sub><sup>2-</sup>--by the weight method in the form of BaSO<sub>4</sub>, HCO<sub>3</sub><sup>-</sup>--by titration according to Ruppin, K<sup>+</sup>--by the cobalt nitrite method, Ca<sup>++</sup> by the weight oxalate method after two and three reprecipitations, Mg<sup>++</sup> was determined in the form Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

The freezing-out tests were conducted in special thermostats filled with a solution of calcium chloride in which the low temperature was maintained by the operation of a refrigerating carbonic acid device. For convenience in operation, two methods were provided for maintaining the low temperatures in the thermostats: by way of direct evaporation of carbon dioxide in coils running in the central distributing tank and by means of supplying this tank with a cold calcium chloride brine from a spare tank, i.e. a "cold storage".

In Fig. 2, we have presented the system of thermostats. The cold brine enters from the central tank (No. 2) into the operating tank (tank No. 1) along tube K<sub>3</sub> while the worm conveyor pumping the warm brine in

the reverse direction through tube  $K_2$  is functioning. Motor M causing the warm conveyor to turn, along with heater H, is activated and deactivated automatically by the thermal control device, T. The mixing in the operating cylinder of the glass mixer is accomplished by means of a friction drive of the movement from the central tank mixer. In the diagram, we do not indicate the second thermostat or the "cold storage" situated in the engine room.

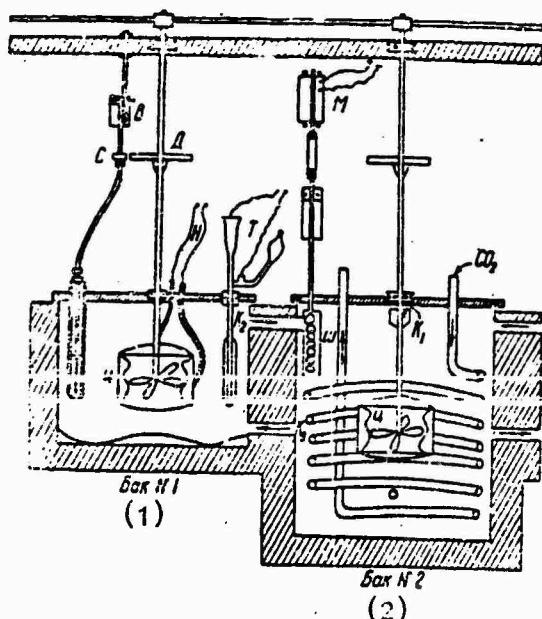


Fig. 2. Key: 1. Tank No. 1; and 2. Tank No. 2.

In this manner, we obtained data from three series of tests: 1) cooling of sea water during intensive mixing for 2-3 days with the introduction, into the solid phase of the surplus of salts being separated (equilibrium states); 2) prolonged (up to four weeks) freezing-out of sea water without mixing and 3) freezing-out of a solution of the sea water type, lacking in  $\text{CaSO}_4$ .

The results of a thermal analysis of sea water and its concentrates obtained by us with the method of cooling curves are presented in Table 4, containing the values of temperature levels corresponding to the beginning of salt separation (K. E. Gitterman and V. F. Korolev). These data are reflected in Fig. 3 illustrating in a very graphic manner the process of sea water's cooling.

On the horizontal axis, there are plotted the values for the concentration factor ( $K$ ) of solutions determined by the relative content of constant component, i.e. Mg ion. On the vertical axis, the temperature is plotted. The equilibrium curves divide the diagram into eight areas: I- area of ice separation; II- area of combined crystallization of ice and Glauber's salt;

III- area of ice separation, Glauber's salt and sodium chloride bihydrate; IV- area of crystallization of Glauber's salt; V- area of combined separation of sodium chloride bihydrate and Glauber's salt; VI- area of crystallization of sodium chloride and Glauber's salt; VII- area of crystallization of sodium chloride and VIII- unsaturated solutions. Boundaries of areas I-II and IV-VIII are represented by two lines. The top (broken) line pertains to the case when the concentrates of normal composition are subjected to cooling; the lower line characterizes the temperature limit of the separation of Glauber's salt from the solutions of the type of sea water not containing  $\text{CaSO}_4$ . With an increase in the concentration of solutions, these curves gradually merge, since the solubility of calcium sulfate decreases. In the concentrates of sea water saturated with common salt, the solubility of  $\text{CaSO}_4$  is so slight that the curves merge together.

The diagram indicates the parameters of the cooling process of various concentrates of ocean water and permits us to make a number of significant conclusions. In the cooling of sea water of the composition indicated above at a salinity to  $-1^{\circ} .8\text{C}$ , ice crystallization begins. At a further freezing-out, the separation of ice occurs so intensively that at  $-5^{\circ}$ , the system has a pasty consistency. The more concentrated solutions begin to separate ice at temperatures decreasing correspondingly, which are located on curve ABB<sup>1</sup>. At point B<sup>1</sup>, there occurs a simultaneous crystallization of ice and Glauber's salt. To this point, there corresponds a solution which is 3.5 times more concentrated than sea water. The analogous point B corresponds to a solution not containing  $\text{CaSO}_4$ , with the concentration factor  $K = 4$ . The concentrates of a higher multiplicity to  $K = 8.85$  separate the Glauber's salt during cooling of a first solid phase. The corresponding temperature points lie on curve B<sup>1</sup>C for solutions of normal composition and on curve BC for the same solutions not containing  $\text{CaSO}_4$ . At a further cooling of these concentrates, as the second solid phase, there will be separated either ice, i.e. the points belonging to the line B BG (for the solutions with a multiplicity ranging from  $K = 3.5$  to  $K = 7.29$ ) or sodium chloride bihydrate, if the appropriate vertical lines intersect line IG. For the last solutions, ice proves to be the third solid phase. The solutions available according to the values of concentration factors to the right of line CD, are located in the area of crystallization of cooking salt and are saturated by it. The cooling of these solutions leads to a separation of Glauber's salt as a second phase at temperatures established by curve CE (or of magnesium sulfate, for the higher concentrates). At their further cooling, there occurs a transformation to a solid phase: sodium chloride converts to bihydrate; line IK forms the temperature boundary of this transformation.

The efforts made to establish, with the thermal analysis procedure, the crystallization temperature of calcium carbonate proved fruitless; we describe below the behavior of this salt during the freezing-out of sea water. It is known that in water free of  $\text{CO}_2$ , the solubility of calcium carbonate is very low; various researchers report fluctuating values for the product of solubility of this salt, on an average established as the

value  $5 \cdot 10^{-9}$ , which corresponds to around 16 mg of  $\text{CaCO}_3$  per liter of solution. The basic factors influencing the solubility of calcium carbonate in water are: partial pressure of carbon dioxide in the above-solution space, temperature and concentration of hydrogen ions, determined by the pH-value. In the presence of  $\text{CO}_2$ , the solubility of calcium carbonates increases intensively as a result of the formation of the more soluble calcium bicarbonate. Under the effect of the  $\text{CO}_2$  present in air (partial pressure  $P_{\text{CO}_2} \approx 3.0 \cdot 10^{-4}$  atm), the solubility of  $\text{CaCO}_3$  is raised to 61 mg per liter of solution. In case of dissolving  $\text{CaCO}_3$  in sea water, the question is complicated by the presence of incidental salts, in which calcium sulfate reduces, while the remaining salts favor the solubility of  $\text{CaCO}_3$ . In view of the basic importance of studying the carbonate equilibria in ocean water, extensive literature, collected in the outstanding monograph by Wattenberg [See Note] has been devoted to this question ([Note]: H. Wattenberg. "Scientific Results of German Atlantic Expedition on the 'Meteor'", Vol. VIII, Berlin, 1933). According to Dittmar, the average  $\text{CaCO}_3$  content in 130 samples of sea water comprises 0.124 g/l. Wattenberg studied the  $\text{CaCO}_3$  sea water system at 25°C and found a dependence of calcium carbonate's solubility on  $P_{\text{CO}_2}$  and pH of the solution. Furthermore, having utilized the temperature coefficients determined by Buch and co-workers (1932) for the constants of carbonic acid, with the aid of the latest physico-chemical concepts, Wattenberg extended his results in the following ranges of variables: temperature from 0° to +30°, pH from 7.3 to 8.5;  $P_{\text{CO}_2}$  from  $0.5 \cdot 10^{-4}$  to  $10 \cdot 10^{-4}$  atm. Comparing

the data derived with the most reliable analyses of sea water, Wattenberg concludes that ocean water is persistently oversaturated with calcium carbonate.

Table 4  
TEMPERATURES (°C) LEVELS ON COOLING CURVES OF SEA  
WATER CONCENTRATES NOT CONTAINING  $\text{CaSO}_4$

(1) № остановки	(2) К о н ц е в т р а т ы											
	1	2	3	4	5	6	7	8	8.5	9	10	11
1	-1.8	-3.8	-6.0	-8.5	-5.6	-3.5	-2.1	-1.0	-0.6	-0.3	+0.2	+0.5
2	-	-	-8.6	-8.7	-12.1	-15.7	-20.6	-12.1	-5.2	-22.9	-2.2	-2.4
3	-	-	-	-	-22.4	-22.3	-22.5	-22.6	-	-23.1	-	-

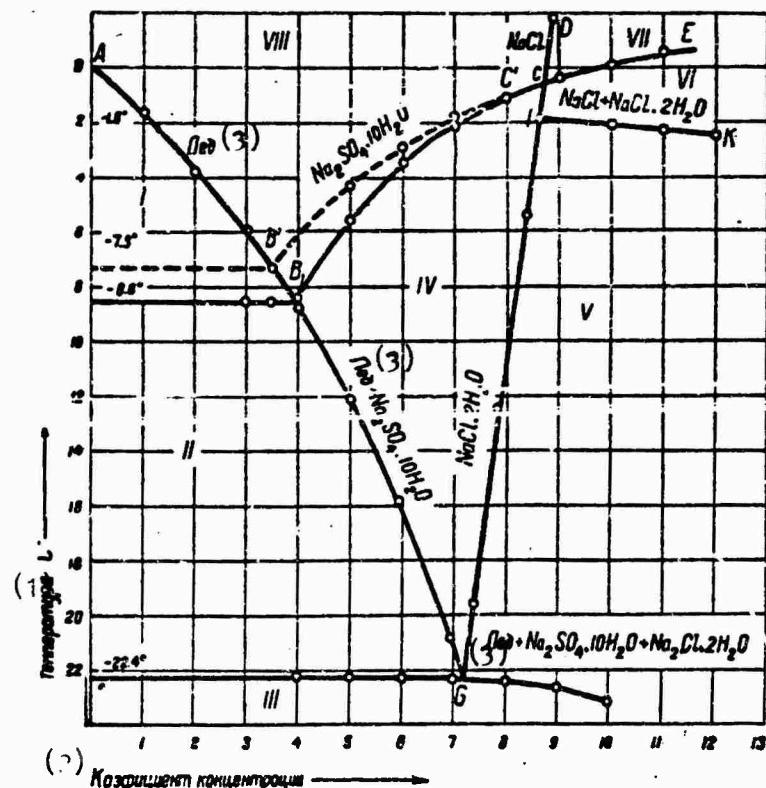
Key: 1. no. of stop (level); 2. concentrates.

Table 4a

TEMPERATURES ( $^{\circ}\text{C}$ ) OF STOPS FOR SOLUTIONS CONTAINING  $\text{CaSO}_4$ 

(1) № остановки	Концентраты (2)			
	3.5	5	6	7
1	-7.3	-4.3	-2.9	-1.8
1	-8.5	-	-	-
3	-	-	-	-

Key: 1. no. of stop; and 2. concentrates.

Fig. 3. Key: 1. temperature  $t$ ; 2. concentration factor; 3. ice.

In our report, we were interested in the behavior of calcium carbonate during the cooling and freezing-out of sea water and its concentrates. For the tests, we used chemically pure calcium carbonate which was loaded into the cylinder with the test solution. Mixing of the system was achieved by suction of atmospheric air, in which the elasticity of  $\text{CO}_2$  fluctuated in a narrow range of around  $P_{\text{CO}_2} = 3.0 \cdot 10^{-4}$  atm. Before reaching the solution, the air passed through a long coil inserted in a thermostat and was cooled to a given temperature. The test was conducted for 9 days, during which every 2 days, we took a sample of the solutions and it was established that after 3 days, the solution sustains negligibly small variations.

According to McCoy's and Smith's data, equilibrium is established in 2-3 days, while Wattenberg's observation indicates that even after 24 hours, the  $\text{CaCO}_3$  solubility does not change ( $t^{\circ} = 20^{\circ}$ ). We tested another way for approaching an equilibrium state, i.e. from the aspect of supersaturation. We passed carbonic gas for about 5-6 minutes through a solution with a  $\text{CaCO}_3$  precipitate. A significant part of the  $\text{CaCO}_3$  became dissolved, converting to  $\text{Ca}(\text{HCO}_3)_2$ . Then we pumped atmospheric air through the solution for 8-9 days and we observed the changes occurring in the liquid phase. In this connection, we found that the values derived for the solubility of  $\text{CaCO}_3$  proved to be quite fortuitous (depending on intensity and time of  $\text{CO}_2$ 's passage) and clearly exaggerated up to 200-300% as compared with the results obtained at gradual saturation of the solution by calcium carbonate. We have shown in Table 5 the solubility of  $\text{CaCO}_3$  in sea water concentrates at various temperatures (K. E. Gitterman and M. M. Vil'ner).

Table 5

SOLUBILITY OF  $\text{CaCO}_3$  IN SEA WATER DEPENDING ON SALINITY AND TEMPERATURE  
 $(P_{\text{CO}_2} \approx 3.0 \cdot 10^{-4}$  atm).

$\frac{(1) \text{Temperatura} (\text{C})}{\% \text{Cl}'}$	-1.8	-3.5	-4.8	-7.4
18.5	0.114	—	—	—
37.0	0.099	0.094	—	—
45.0	0.093	0.086	0.082	—
55.5	0.084	0.073	0.071	—
65.0	0.077	0.067	0.062	0.056

Key: 1. Temperature ( $^{\circ}\text{C}$ ).

Examining the individual isotherms, we can conclude that with an increase in the salinity of the solutions, the solubility of calcium carbonate decreases. A drop in temperature operates in the same direction; this contradicts the general trend of the solubility curves theoretically derived by Wattenberg who, basing his calculations on an increase in the coefficient of  $\text{CO}_2$  absorption at a drop in temperature, did not consider that this factor is counteracted by the positive temperature factor of  $\text{CaCO}_3$  solubility revealed in the solutions free of  $\text{CO}_2$ . It can be postulated that at a certain partial pressure of  $\text{CO}_2$  in the above-solution space, the variation in temperature in a narrow range will not be reflected on the solubility of calcium carbonate, since a compensation of opposing factors will occur: at an increase in temperature, there will be a slight reduction in absorption of  $\text{CO}_2$  by the solution, which will involve the dissociation of the corresponding amount of bicarbonate, but in view of the increase in the solubility of  $\text{CaCO}_3$ , its separation will not occur.

Without special assumptions, it is difficult to make a detailed comparison of the  $\text{CaCO}_3$  solubility values obtained by us for relatively concentrated solutions, with those calculated by Wattenberg; we present in Table 6 the variation in the solubility of calcium carbonate in the process of cooling and freezing-out of sea water; based on the values obtained for the solubility of  $\text{CaCO}_3$ , we have computed the extent of its separation at various temperatures in relation to the content of carbonate in the solution cooled to inception of ice crystallization.

Table 6

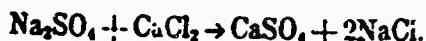
SOLUBILITY AND EXTENT OF SEPARATION OF  $\text{CaCO}_3$  DURING FREEZING-OUT OF SEA WATER  
 $(F_{\text{CO}_2} \approx 3.0 \cdot 10^{-4} \text{ atm})$

(1) No. по пор.	(2) Темпе- рату- ра (°C)	Cl (‰)	$\text{CaCO}_3$ (‰)	(3) Степень выделе- ния $\text{CaCO}_3$	(4) Твердая фаза	(5) Причесание
1	+15.0	15.5	0.124	—	$\text{CaCO}_3$	{ (6) Диттмар (средн. из 130 приб.)
2	+15	19.5	0.067	—	$\text{CaCO}_3$	{ (7) Рассчитано по Ваттенбергу
3	0	19.5	0.090	—	$\text{CaCO}_3$	
4	0	18.5	0.110	—	$\text{CaCO}_3$	
5	-1.6	18.5	0.114	—	$\text{CaCO}_3$	{ (8)
6	-3.5	37.0	0.094	53.8	$\text{CaCO}_3$	{ Гиттерман и Вильнер (опытные
7	-4.8	45.0	0.082	70.1	$\text{CaCO}_3 + \text{жел}$	{ данные)
8	-7.4	65.0	0.056	86.0		

Key: 1. No. in series; 2. Temperature, °C; 3. Extent of separation of  $\text{CaCO}_3$ ; 4. Solid phase; 5. Remarks; 6. Dittmar (average of 130 samples); 7. Calculated according to Wattenberg; and 8. Gitterman and Vil'ner (experimental data).

In this manner, at the freezing-out of sea water to  $-3.05^{\circ}\text{C}$  ( $370/\text{oo}$ ), around 59% of the calcium carbonate is precipitated. At further cooling, the intensity of its release decreases somewhat: at  $-70.4$ , 14% of  $\text{CaCO}_3$  will remain in the solution.

At a temperature of  $-70.3^{\circ}\text{C}$ , crystallization of Glauber's salts begins and the solution sustains appreciable variations in its composition. We have collated in Tables 7, 8 and 9 the resulting material permitting us to trace the gradual metamorphization of sea water, as well as the order, composition and quantity of salts being separated. At a further drop in temperature, the incipient crystallization proceeds extremely intensively. The separation of  $\text{SO}_4^{2-}$  in the form of Glauber's salt comprises around 59% at  $-100$ ; around 84% at  $-15^{\circ}$ , of the  $\text{SO}_4^{2-}$  content in sea water. Around  $-15^{\circ}$ , the solution is saturated by calcium sulfate and at further cooling, interaction of the solid and liquid phases occurs, consisting of a partial transformation of the sodium sulfate into calcium sulfate according to the following reaction:



In this manner, in the stage of the process being described, the composition of solid phases includes (in addition to calcium carbonate) sodium and calcium sulfates. At a temperature of  $-22^{\circ}.4$ , sodium chloride is added to them, crystallizing in the form of  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ . From this moment, the total concentration of the solution (% of total salts) occurs gradually, as this also takes place in the evaporation of sea water in the stage of precipitation of sodium chloride.

We have shown in Fig. 4. the path for the crystallization of salts in the process of freezing-out the sea water. The base of the diagram is formed by the sector of horizontal projections of various isotherms of the  $\text{NaCl}-\text{MgSO}_4-\text{H}_2\text{O}$  system. In the calculation of indexes according to Le-Chatelier-Jeneke, we tentatively excluded  $\text{CaCl}_2$  from the composition of the solutions and the difference in gram-equivalents ( $\text{Cl}^- + 1/2 \text{SO}_4^{2-}$ ) —  $1/2 \text{Mg}^{++}$  was adopted for the gram-equivalent of sodium ( $\text{Na}^+$ ).

The point of the composition of sea water at low temperatures lies in the field of Glauber's salt. The incipient crystallization of this salt causes the corresponding movement of a symbolic point along the path of  $\text{Na}_2\text{SO}_4$ . Around  $-22^{\circ}.6$ , the crystallization path is distorted as a result of the precipitation of sodium chloride bihydrate, where the relative composition of crystallizing salts is determined for each point of an appropriate tangent derived for the side ( $\text{Na}_2\text{Cl}_2-\text{Na}_2\text{SO}_4$ ) of a Jeneke square. The following concentrates are located on the diagram path originating from a point quite close to the  $\text{NaCl}$  pole, i.e. during this period, the crystallization of almost pure sodium chloride bihydrate occurs.

Table 7

## SUCCESSIVE FREEZING—OUT OF SEA WATER

(1) №	Temper. (°C)	Kоnсtп. K	(4) Concentration factors (e.c.)						(5) Jeneke indexes			
			Cl'	SO <sub>4</sub>	Mg <sup>++</sup>	Ca <sup>++</sup>	K	Na <sup>+</sup>	KCl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaSO <sub>4</sub>
1	-1.8	1.00	1.84	0.260	0.125	0.030	—	2.31	—	0.401	0.100	0.385
2	-5.6	2.95	5.24	0.740	0.350	0.100	—	6.00	—	1.300	0.277	1.017
3	-7.6	3.45	6.72	0.910	0.400	0.120	—	8.49	—	1.760	0.833	1.347
4	-9.5	4.31	7.94	0.596	0.539	0.124	—	10.16	—	2.111	0.344	0.881
5	-10.6	4.76	8.76	0.505	0.504	0.105	—	11.10	—	2.338	0.458	0.747
6	-12.3	5.35	9.67	0.390	0.614	0.190	—	11.70	—	2.626	0.527	0.585
7	-15.0	5.80	10.85	0.250	0.750	0.188	—	13.72	—	2.944	0.521	0.377
8	-17.0	6.55	12.0	0.190	0.812	0.165	—	15.40	—	3.187	0.514	0.211
9	V-22.6	8.47	14.95	0.161	1.06	0.149	0.810	17.65	0.59	4.16	0.414	0.233
10	-24.2	14.4	14.50	0.181	1.80	0.131	0.641	14.04	1.03	7.05	0.364	0.218
11	-26.0	20.3	14.82	0.248	2.54	0.126	0.740	10.64	1.43	9.96	0.350	0.167
12	-28.0	24.5	15.31	0.301	3.06	0.118	0.950	8.74	1.87	12.01	0.328	0.445
13	-30.8	25.5	15.89	0.410	3.69	0.091	1.14	6.44	2.18	14.47	0.262	0.666
14	-32.2	32.1	16.49	0.170	4.01	0.672	1.26	6.11	2.41	15.72	0.200	0.095
15	-34.2	36.7	16.52	0.594	4.52	0.055	1.04	3.65	2.08	17.74	0.153	0.878
16	-35.6	38.1	16.81	0.120	4.77	0.032	0.94	3.21	1.79	18.70	0.085	1.065

Key: 1. No. of experiment; 2. Temperature, eC; 3. Concentration factor, K; 4. Composition of liquid phase (% by weight); 5. Total salts; and 6. Jeneke indexes [Read other headings as they are]

Table 8

## SALT BALANCE IN PROCESS OF FREEZING-OUT OF SEA WATER

(1) п з 2	(2) Temper. (°C)	(3)		(4)					
		(3a) жидк.	(3b) твёрд.	H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	CaSO <sub>4</sub>	NaCl	KCl	MgCl <sub>2</sub>
1	-0	1000.0	-	-	-	-	-	-	-
2	-1.8	1000.0	-	-	-	-	-	-	-
3	-5.5	351.8	648.2	648.2	-	-	-	-	-
4	-7.8	273.6	726.4	78.0	0.16	-	-	-	-
5	-9.5	231.9	768.1	40.1	1.65	-	-	-	-
6	-10.6	209.6	790.4	21.8	0.47	-	-	-	-
7	-12.8	191.0	809.0	18.2	0.46	-	-	-	-
8	-15.0	169.3	830.7	21.1	0.32	0.15	-	-	-
9	-17.0	152.6	847.4	13.7	-0.04	0.11	-	-	-
10	-22.6	117.6	882.4	32.3	-0.09	0.36	2.47	-	-
11	-24.2	68.8	931.3	27.3	-0.24	0.24	11.43	-	-
12	-26.0	43.9	951.1	15.5	-0.08	0.10	4.40	-	-
13	-28.0	40.4	959.6	6.7	-0.15	0.05	1.80	-	-
14	-30.8	23.6	966.4	5.5	-0.09	0.02	1.30	-	-
15	-32.2	32.7	967.3	1.2	-0.05	0.03	0.70	-	-
16	-34.2	27.4	972.6	3.7	-0.04	0.02	0.52	0.13	-
17	-35.5	25.8	974.2	1.2	-0.01	0.02	0.28	0.10	-
(5) Выделялось солей (г)		947.5	2.37	1.20	22.90	0.23	0.00		
(6) Остаток солей в жидкой фазе (г)		19.4	0.21	0.03	0.85	0.46	4.85		
(7) Сумма солей (г)		966.9	2.58	1.23	23.75	0.69	4.85		

Key: 1. No. of points; 2. Temperature, °C; 3. Relationship of phases (g); 3a. liquid; 3b. solid; 4. Composition and quantity of salts (g per kg of sea water); 5. Salts released (g); 6. Residue of salts in liquid phase (g); and 7. Total salts (g).

The typical bending of the path in the direction of magnesium sulfate (also expressed for lines of dual equilibrium  $\text{NaCl} \cdot 2\text{H}_2\text{O} - \text{Na}_2\text{SO}_4 \cdot 10\text{ H}_2\text{O}$  of superjacent isotherms) is explained by the increased solubility of Glauber's salt, evoked by an increase in the magnesium chloride concentration and by the precipitation (from the solution) of an analogous ion  $\text{Na}^+$  in the form of  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ . The relative amount of the precipitated sodium chloride and of dissolved sodium sulfate for any point in this sector of the crystallization path is determined by a tangent drawn to the intersection with the extension of side  $\text{Na}_2\text{Cl}_2$  of the Jeneke square. Additional freezing-out was not conducted but it can be envisioned that the last experimental point lies near the incongruent point of the combined crystallization of ice, sodium chloride

bihydrate and sodium and magnesium sulfates. In the case of a sufficient quantity of Glauber's salt in the solid phase, at this point there would have developed a complete freezing of the solution; however, since the molar content of a magnesium ion in sea water exceeds the same for an  $\text{SO}_4^{2-}$  ion, a decrease in temperature leads to the processing of the Glauber's salt to dodecahydrate of magnesium sulfate ( $\text{MgSO}_4 \cdot 12 \text{H}_2\text{O}$ ) and to the disappearance of the liquid phase only in the point of magnesium chloride's ( $\text{MgCl}_2 \cdot 12 \text{H}_2\text{O}$ ) precipitation. The obtainment of equilibrium states in this sector of the polytherm is quite difficult owing to the hindered state of the interphase processes, which is explained in turn by the solutions' high viscosity and by the inactivity of the molecules and ions, the hydration of which increases greatly with a decline in temperature.

Table 9

EXPERIMENTS IN PROLONGED FREEZING-OUT OF SEA WATER WITHOUT MIXING

(1) No. of test	(2) Temperature, °C	(3) Состав жидкой фазы (вес. %)										% выделения в (5) твердой фазы от содержания в мор- ской воде		
		C	$\text{SO}_4^{2-}$	Mg	N	NaCl	Mg	$\text{CaCl}_2$	$\text{MgSO}_4$	$\text{CaSO}_4$	Other salts	H <sub>2</sub> O	$\text{SO}_4^{2-}$	H <sub>2</sub> O
1	-5.8	5.42	0.755	0.372	0.115	7.14	1.460	-	0.708	0.391	9.70	90.30	1.54	68.3
2	-9.6	8.28	0.510	0.567	0.160	10.92	2.223	-	0.186	0.544	13.87	86.13	56.5	80.4
3	-9.9	8.15	0.516	0.550	0.155	10.79	2.155	-	0.213	0.527	13.66	86.32	55.4	79.8
4	-10.5	8.45	0.520	0.575	0.171	11.16	2.255	-	0.161	0.582	14.15	85.85	56.5	80.7
5	-11.3	9.05	0.481	0.615	0.172	11.95	2.415	-	0.099	0.586	15.05	84.95	62.4	82.1

Key: 1. No. of test; 2. Solution temperature, °C; 3. Composition of liquid phase (% by weight); 4. Total salts; and 5. % of separation into solid phase of content in sea water.

We have shown in Fig. 5 the phase relationship at freezing-out of sea water. The relative growth of the solid phase proceeds with a gradual delay and intensifies during the stage of  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  precipitation. For the last experimental point, for 1 kg of sea water we obtain 974 g of solid phase and 26 g of solution.

The presence of calcium salts in the system is important in two freezing-out stages: during the precipitation of Glauber's salt prior to the inception of sodium chloride's crystallization and in the final stage of the magnesium sulfate's crystallization.

We have already directed attention above to the development of the reaction:  $\text{CaSO}_4 + 2 \text{NaCl} = \text{Na}_2\text{SO}_4 + \text{CaCl}_2$  in the process of cooling. During

the evaporation of sea water, in the range of standard temperatures, the equilibrium between these salts is shifted to the left all the way to total precipitation of calcium sulfate. In the case of freezing-out, with a temperature drop, equilibrium is shifted to the right, and sodium sulfate is precipitated. In the program at the Institute of Metallurgy on the study of deep cooling of sea water, conducted under the general supervision of Prof. V. P. Il'inskiy, V. F. Korolev [See Note] studied the polythermal area of Glauber's salt crystallization in the system described from -3.0 to -21°.6. ([Note]: V. F. Korolev, "Equilibrium States in  $\text{CaSO}_4$  -  $\text{NaCl}$  -  $\text{H}_2\text{O}$  System").

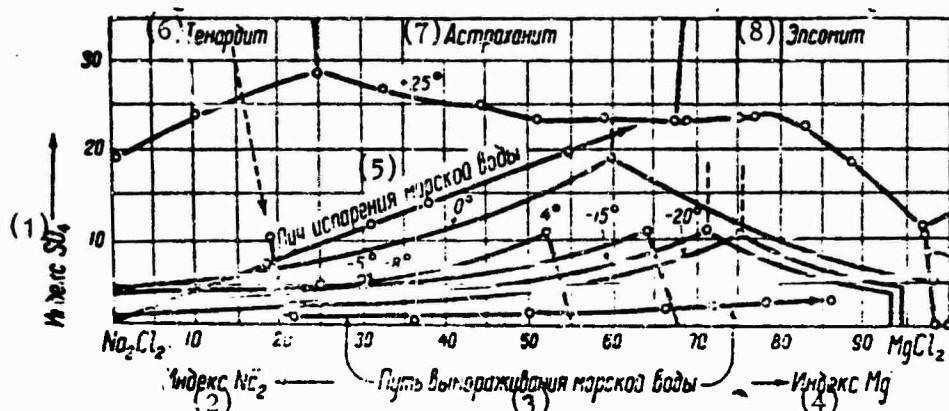
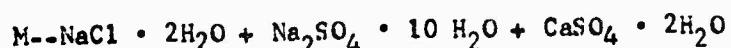
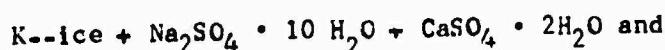


Fig. 4. Key: 1. Index  $\text{SO}_4$ ; 2. Index  $\text{Na}_2$ ; 3. Path of freezing-out of sea water; 4. Index  $\text{Mg}^{++}$ ; 5. evaporation of sea water; 6. Tenardite; 7. Astrakanite; and 8. Epsomite.

In Fig. 5 in V. F. Korolev's report included in the present collection, he has portrayed a part of this system in a Jeneke square. The broken lines indicate the fields' boundaries at -5°.0. A large part of the diagram has been made as an ice area. The development of an ice field proceeds from the poles of  $\text{Na}_2\text{SO}_4$  and  $\text{CaSO}_4$ . There occurs parallelly a compression of the area for crystallization of  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  as a result of the growth of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  fields, wherein the points of ternary equilibrium



with a drop in temperature approach each other and merge at -21°.6; at this moment, we have the coexistence of four solid phases and a further drop in temperature leads to a disappearance of the solution if the molar relationship is such that the amount of  $\text{CaCl}_2$  in the liquid phase is less than the quantity of  $\text{Na}_2\text{SO}_4$  in the solid phase. Otherwise, there will occur a complete reprocessing of Glauber's salt based on the reaction:  $\text{CaCl}_2 + \text{Na}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{NaCl}$  and the number of solid phases will decrease to three.

According to this modification, the complete solidification of the system will develop at the cryohydric point  $\text{CaCl}_2 - \text{H}_2\text{O}$ , i.e. at around  $-55^\circ\text{C}$ .

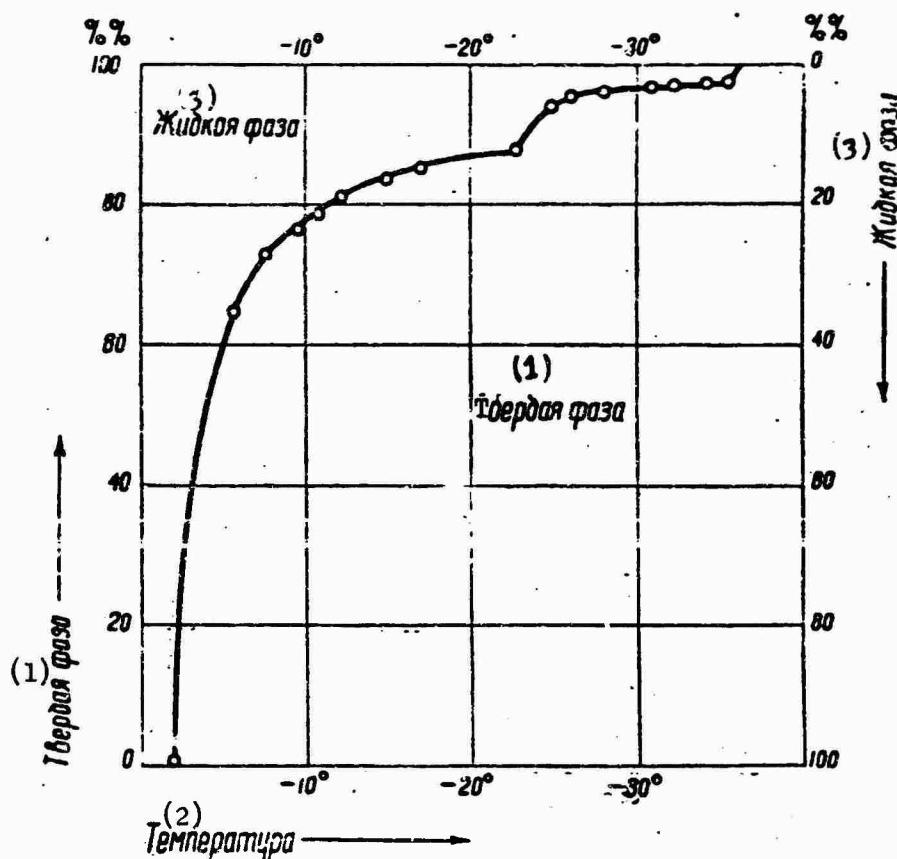
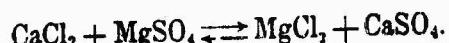


Fig. 5. Key: 1. Solid phase; 2. Temperature; and 3. Liquid phase.

It follows from the phase equilibria that for a four-component solution of  $\text{CaCl}_2 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ , at a molecular relationship of the  $\text{Ca}^{++}$  and  $\text{SO}_4^{--}$  ions, such as occurs in sea water, complete freezing should set in at  $-21^\circ\text{C}$ ; however, in the presence of magnesium chloride, the solution's freezing-out will proceed further and in the subsequent stage of the process, the calcium salts lose their significance and the primary role is assumed by the above-described reaction of the mutual pair  $\text{MgSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ ; in the case of a rise in the molar concentration of  $\text{Ca}^{++}$  above  $\text{SO}_4^{--}$ , at the point of magnesium chloride's crystallization there should again be manifested the effect of calcium salts according to the resultant reaction:



After the reprocessing of the precipitated magnesium sulfate into gypsum, the solution can be subjected to a further freezing-out, all the way to its disappearance in "cryo-eutonics" i.e. around  $-52^\circ\text{C}$  [See Note]; however, in

sea water and its concentrates, the molar content of  $\text{Ca}^{++}$  is less than  $50\text{''}_4$  and hence the final point of the solution's existence corresponds to the precipitation temperature of  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ . In sea water, the presence of small amounts of potassium salts does not alter the overall pattern of the discussion. It is evident from Table 8 for the salt balance that the crystallization of potassium chloride begins directly below  $-33^\circ\text{C}$  ([Note]: Prutton and Tower, Journal of American Chemical Society, 54, 3040, 1932). The authors studied the system  $\text{CaCl}_2 - \text{MgCl}_2 - \text{H}_2\text{O}$  at  $0^\circ$ ,  $-15^\circ$ ,  $-30^\circ$  and found that complete freezing develops at  $-52.0^\circ\text{C}$ .

In this way, we have collected and developed experimental material typifying the process of sea water's freezing-out. The analysis made of the phenomena occurring during the cooling of ocean water could prove useful in studying life in the arctic seas. Comparing our data with Ringer's, we are able to conclude that this researcher failed to consider the reversible processes developing during freezing-out. This was the outcome of a procedural error, consisting in a periodic separation of the solution from the solid phases; as a result, the interphase reactions could not take place. Conducting an artificial separation of the solution from the solid phases, Ringer converted sea water to a class II solution and established the "cryo-eutonics" corresponding to the crystallization temperature of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . We have noted a high value of the reaction of dual exchange of  $\text{CaSO}_4 + 2\text{NaCl} \rightleftharpoons \text{CaCl}_2 + \text{Na}_2\text{SO}_4$ , having in the first stage of freezing-out an orientation from left to right, while from the moment of crystallization of  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ , the trend is reversed. As a result of this, the calcium ion is practically eliminated from the solution's composition and the system's "cryo-eutonics" corresponds to the crystallization temperature of  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ .

The technological significance of the study completed consists in the obtainment of numerous design factors of the freezing-out process collated in the salt balance table (Table 8). Under the proper climatic and natural-geographic conditions, the freezing-out of natural salt brine can form the technical method for their concentration and enrichment.

#### CONCLUSIONS

1. We have accomplished a technical analysis of ocean water from  $0^\circ$  to the temperature of complete freezing.
2. We have established the crystallization temperature of salts for sea water and its concentrates, and have formulated a polythermal diagram typifying the cooling process (Fig. 3).
3. We have made a quantitative evaluation of the behavior of the essential salt components at the freezing-out of sea water, presented in the salt balance table (Table 8).
4. We have identified the presence of the interphase processes having primary significance and explained by the exchange reaction:  $\text{CaSO}_4 + 2\text{NaCl} \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{CaCl}_2$ .

5. Finally, we have investigated the polythermal range of Glauber's salt crystallization in the  $\text{CaSO}_4\text{--NaCl--H}_2\text{O}$  system (V. F. Korolev), in which the results obtained confirm the concepts previously expressed.